Fluctuation-induced pseudogap in thin conventional superconducting films

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A superconducting state is characterized by the gap in the electronic density of states (DOS) which vanishes at the superconductor transition temperature T_c. It was discovered that in high temperature superconductors (HTS) a noticeable depression in the density of states still remains even at temperatures above T_c; this feature being called *pseudogap* [1, 2, 3, 4]. Here we show that a pseudogap exists in a conventional superconductor: ultrathin titanium nitride films in the vicinity of the disorder-driven superconductor-insulator transition (D-SIT) [5, 6], over a surprisingly wide range of temperatures above T_c. We demonstrate that this pseudogap results from quasi-two-dimensional superconducting fluctuations enhanced by the closeness to the disorder-driven superconductor-insulator transition. A general character of the observed phenomenon offers new insight into the origin of the pseudogap state in the layered HTS compounds.

To examine the possibility of the existence of a HTS-like pseudogap in the density of states of conventional superconductors, we have probed the DOS of titanium nitride (TiN) thin films with a Scanning Tunneling Microscope (STM) cooled down in a dilution refrigerator (see methods). The DOS, $\nu(\eta)$ was found as a function of the single electron excitation energy (relative to the Fermi level), $\eta = E - E_F$, and of the temperature T via recording the differential conductance $G(V) = dI/dV$ of the tunneling junction between the STM tip and the sample versus its voltage bias V and using the relation $G(V,T) \propto \int d\eta\, \nu(\eta,T)\,[-(\partial f_T/\partial\eta)(\eta - eV)]$ where f_T was the Fermi distribution at temperature T [2].

We carry out the measurements on three thin film samples, TiN1, TiN2, and TiN3. Their thickness $d \leq 5\,\mathrm{nm}$, is well smaller than the superconducting coherence length $\xi_s \geq 9\,\mathrm{nm}$, implying that our samples are two-dimensional superconductors [7]. The films exhibit the disorder-driven superconductor-insulator transition [6]. The tunable measure of disorder is the film sheet resistance $R_\Box = \rho/d$ where ρ is the resistivity (see Methods). At room temperature $R_\Box = 2.44\,\mathrm{k\Omega}$, $2.70\,\mathrm{k\Omega}$ and $3.47\,\mathrm{k\Omega}$ for TiN1, TiN2, and TiN3 samples respectively, indicating the high degree of disorder with $k_F l \sim 1$ [8] (k_F is the Fermi wave vector and l the electronic mean free path). The superconducting transitions of all the three samples are shown in Fig. 1a. Raising the degree of disorder, from TiN1 to TiN3, shifts the critical temperature T_c towards zero and broadens the transition. This continuous suppression of T_c with the increasing sheet resistance ($R_\Box$) is characteristic to the disorder-driven SIT in homogeneously disordered superconductors [7, 9, 10].

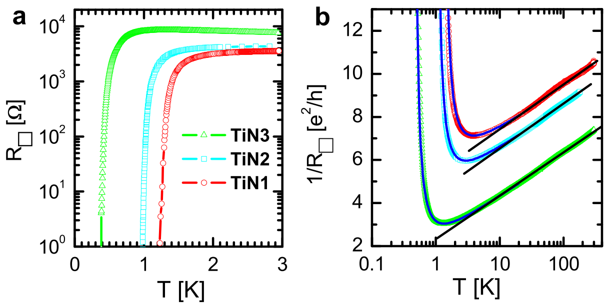

FIG. 1: **Transition to a superconducting state of the TiN films**. **a,** Sheet resistance versus temperature close to the superconducting transition. The critical superconducting temperature T_c is reduced as the disorder increases from TiN1 to TiN3. **b,** dimensionless conductance $g = (h/e^2)R_\Box^{-1}$ measured from room temperature down to T_c. The semi-logarithmic representation reveals the logarithmic reduction of the conductance due to weak localization and Coulomb interaction effects. T_c which equals 1.3 K, 1.0 K and 0.45 K for TiN1, TiN2 and TiN3 respectively, is obtained by fitting the conductance curves with all the quantum corrections to the conductivity (see Ref. [7]). The fits are shown as solid blue lines.

Figure 2 presents our data on the tunneling DOS as three-dimensional plots of the tunneling conductance $G(V, T/T_c)$ vs. voltage bias V and normalized temperature T/T_c. Close to $T = 0$, the DOS of the three samples present a gap centered at the Fermi level, i.e. $V = 0$, with two peaks at the edges which conform well to the standard Bardeen-Cooper-Schrieffer theory of conventional s-wave superconductor [11]. Upon increasing temperature, quasi-particle states begin filling this gap. Although a flat metallic DOS is restored exactly at T_c in a TiN film 100 nm thick, which is well beyond the

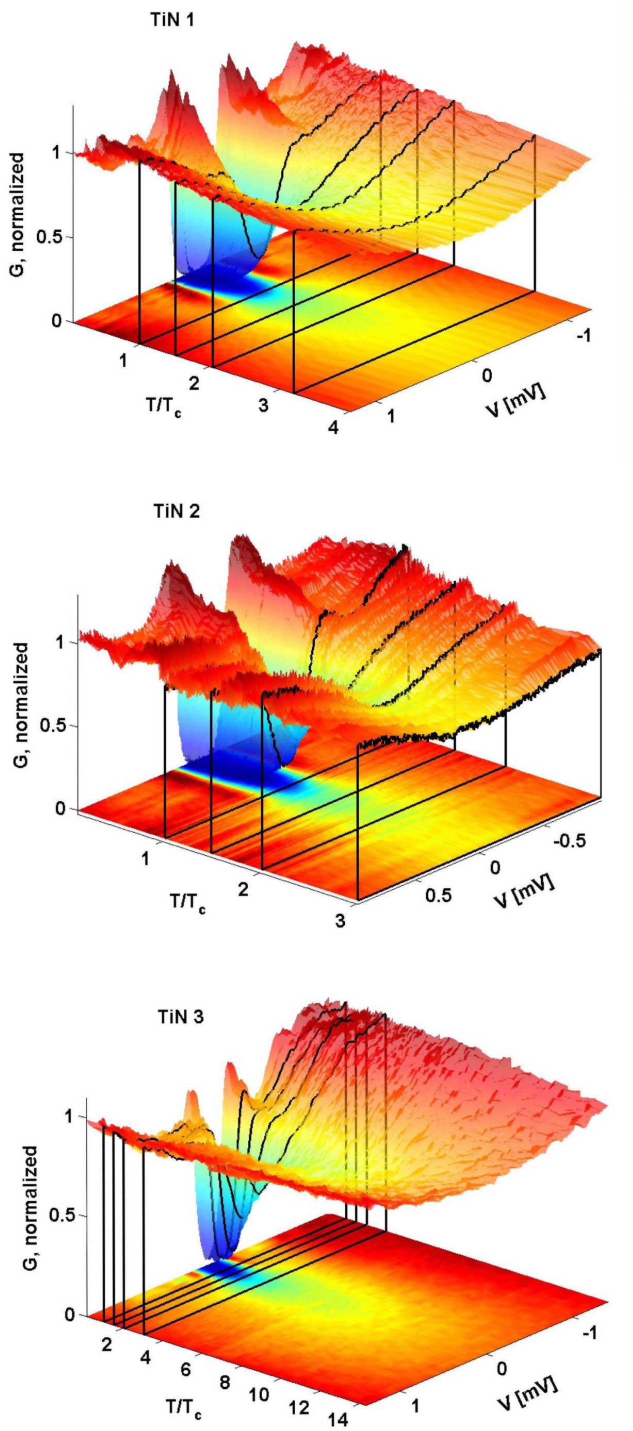

FIG. 2: **Fluctuation-induced pseudogap in the density of states**. Three dimensional plots of the tunneling conductance $G(V, T/T_c)$ normalized by the conductance measured at high voltage and low temperature as a function of bias voltage and normalized temperature T/T_c for TiN1 (top), TiN2 (middle) and TiN3 (bottom). Black lines are spectra measured at $T/T_c = 1, 1.5, 2, 3$ which show that the pseudogap state is all the more pronounced and extended in a relative temperature scale T/T_c for increasing disorder from TiN1 to TiN3. In TiN1, the dip at $V = 0$ is as large as 70 % of $G(V)$ at high bias and reaches 90% in TiN3 where it remains visible at about 14 times T_c.

two-dimensional limit (see supplementary information), the measurements revealed that in thin disordered films under study a striking DOS anomaly persists in a wide temperature range above T_c. When approaching the critical disorder at which the D-SIT occurs, both this temperature range and the depth of this pseudogap increase. This demonstrates that a HTS-like pseudogap anomaly can therefore occur in conventional low-T_c superconductor.

To understand the nature of the observed pseudogap, we attract the data on the transport properties that compliment the direct STM observations of the DOS. Fig. 1b shows in a semi-logarithmic scale the T-dependence of the dimensionless conductance $g = (h/e^2)R_\square^{-1}$. In all the three samples, it decreases logarithmically upon cooling down from the room temperature towards the proximity of T_c, where the noticeable deviation from the logarithmic dependence takes place. We attribute the logarithmic behavior to the usual quantum corrections to the conductivity in quasi-two dimensional diffusive system, namely weak-localization and electron-electron interaction corrections [13, 14, 15].

While there are several effects that are hard to separate from each other that determine the beginning of the upturn of the conductance, on a very approach to T_c, the main contribution comes from the superconducting fluctuations (SF). Their role is two-fold: the onset of the fluctuational Cooper pairs suppresses the DOS at the Fermi level, resulting in an insulating trend in temperature dependence of the resistance, which, thus, *grows* upon decreasing temperature. At the same time, fluctuational Cooper pairs short electronic conductivity, and, as the superconducting fluctuations become developed enough, this shunting effect disguises the suppressing of the DOS.

The effect of suppression of DOS can be exposed by measurements of tunneling conductance. A temperature evolution of the SF-induced suppression of DOS and the resulting change in the *tunneling* conductance has been discussed by Varlamov and Dorin [16] within the framework of the perturbation theory of superconducting fluctuations [17] and is given by the "double-log" temperature dependence:

$$\frac{\delta G}{G}(V = 0, \varepsilon) \simeq 2Gi \ln(\varepsilon) \,. \qquad (1)$$

Here, $Gi \approx (e^2/23\hbar)R_\square$ is the Ginzburg-Levanyuk parameter [17] characterizing the strength of the superconducting fluctuations, and $\varepsilon = \ln(T/T_c)$ is the reduced temperature.

To relate the observed pseudogap to superconducting fluctuations, we have inspected the measured temperature evolution of the differential conductance at the zero bias. As shown on Fig. 3a, the raw data follow Eq. (1) with the high accuracy over the wide temperature range, and the slopes of $\delta G(V = 0, \varepsilon)$ vs. $\ln \varepsilon$ dependencies in-

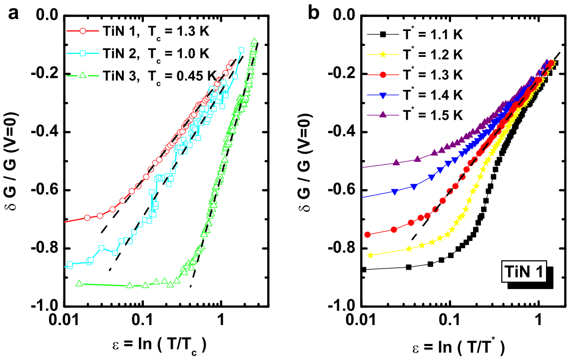

FIG. 3: **Temperature dependence of the zero bias tunneling conductance**. The thermal evolution of $\delta G/G = (G(V=0,\varepsilon) - G_0)/G_0$ the differential conductance relative to its value G_0 at the highest temperature and bias voltage is represented as a function of the reduced temperature $\varepsilon = \ln(T/T_c)$ in a semi-logarithmic plot. **a,** The straight lines accentuate the peculiar double-logarithmic temperature dependence (i.e. as function of $\ln[\ln(T/T_c)]$) of the pseudogap at the Fermi level for each of the three samples. **b,** Illustration of the "no-fitting-parameter" character of our plots. Even the slight modification of T_c (for about 50 mK) would have eliminated the linear dependence of $\delta G/G$ upon $\ln[\ln(T/T_c)]$.

crease with disorder, i.e. with $R_\square$. It is noteworthy that the plots do not contain any adjusting parameter: the value of T_c is independently derived from the transport measurements data. At the same time, $\delta G(V=0,\varepsilon)$ vs. $\ln\varepsilon$ dependence offers an independent method for determining T_c. Indeed, the slightest change in T_c, eliminates the linear dependence of $\delta G/G$ on $\ln\varepsilon$, see Fig. 3b. The plots exhibit a linear dependence of $\delta G/G$ on $\ln\varepsilon$ in a large temperature range only if $T^* = T_c$ within the 50 mK accuracy evidencing a remarkable consistency between the spectroscopic and transport data. In other words, the fluctuation-induced pseudogap probed by STM gives a very straightforward signature of SF through the sole DOS correction which is otherwise entangled in transport measurements with other SF quantum corrections [17].

In spite of the fact that Eq. (1) was derived in the framework of the perturbation theory, it holds over the whole domain of Gaussian fluctuations, $Gi \ll \varepsilon \ll 1$, as long as the condition $\delta G/G \ll 1$ is satisfied. Moreover, Figure 3 shows that the $\ln\varepsilon$ law holds well beyond the perturbative regime extending to the region where the SF corrections are large, and also persist to well far from T_c where $\varepsilon \geq 1$. The other limit ($Gi \ll \varepsilon$) determines the temperature below which one enters the critical region where the fluctuations are correlated and cannot be considered as Gaussian any longer. In Fig. 3, this corresponds to the plateaus where the DOS is nearly temperature independent. As expected from SF theory [17], both the temperature range of this critical regime as well as the slope of the $\ln[\ln(T/T_c)]$ law which follows, increase from the less resistive sample TiN1 to the more resistive one TiN3, reflecting the increase of Gi with disorder.

All the above indicates that the observed pseudogap originates from the superconducting fluctuations of the density of states. To establish this conclusively, one has to examine the role of the Coulomb interactions since they also contribute to suppression of the DOS [13, 14]. The corresponding correction has logarithmic temperature dependence and indeed manifests itself in the logarithmic behavior of the conductance shown in Fig. 1b. However, replotting the data of Fig. 3a as function of $\log T$, does not reveal linear behavior. Therefore the temperature behavior of the DOS at the Fermi level in our films cannot be explained by the Aharonov-Altshuler-Lee zero-bias anomaly which becomes negligible as one approaches T_c because of the much stronger divergence of (1). This is the reason why SF not only dominate the DOS behaviour at E_F but also govern the transport properties at very low voltages.

The conclusions at which we arrive are as follows: First, in clean low-T_c superconductors, $k_F l \gg 1$, the SF regime is limited to a narrow range of temperatures near T_c. On the contrary, in our TiN thin films, the SF-dominated temperature region extends up to temperatures well above T_c. Remarkably, the pronounced pseudogap persists up to the highest temperature achieved in the experiment 6.3 K, which is about 14 T_c for the TiN3 sample. This parallels the recent observations [18] of the Nernst effect generated by the short-living Cooper pairs in $Nb_{0.15}Si_{0.85}$ thin films seen up to $30\,T_c$. The latter material, like our TiN films, is in the vicinity of a two-dimensional D-SIT, thus the enhancement of superconducting fluctuations there should be also assigned to strong disorder. Second, the observed double-log temperature dependence (1) results from the fluctuations of the amplitude of the superconducting order parameter. While the origin of the pseudogap in the high-T_c materials remains a subject of the extensive debate, one of the existing views [19] relates it to the *phase* fluctuations of the order parameter. The Nernst effect in thin superconducting indium oxide thin films [20], organic superconductors [21], and HTSs [22, 23] is often attributed to the same cause. However, in thin films the *phase* fluctuations dominated regime is restricted to a narrow interval of temperatures between the Berezinskii-Kosterlitz-Thouless (BKT) transition temperature $T_{\rm BKT}$, at which the phase coherence is established, and $T_{\rm c}$ [17]. Therefore, phase fluctuations cannot be responsible neither for the origin of pseudogap observed in our work nor for pseudogaps found in other 2D systems. This calls for revisiting our views on the origin of pseudogap (and on the mechanism of the Nernst effect as well), since they also are of a quasi-two-dimensional nature. In particular, the immediate natural question is what is the role of the order parameter *amplitude* fluctuations in HTS properties [2, 24, 25, 26, 27].

In summary, our work presents experimental evidence that the ordinary disordered superconducting films possess the pseudogap resulting from the quasi-two-dimensional superconducting fluctuations of density of states. This offers a new insight into a fascinating pseudogap state in cuprates, which is believed to be a key feature of an underlying mechanism of high temperature superconductivity.

METHODS

Samples. Our samples are ultra-thin films of titanium nitride synthesized by atomic layer chemical deposition onto a Si/SiO_2 substrate. TiN1 is a 3.6 nm thick film deposited at 400°C while TiN2 and TiN3 are 5.0 nm thick films deposited at 350°C. TiN3 was then slightly plasma etched in order to reduce its thickness. Electron transmission and diffraction pattern revealed the films to be made of densely-packed crystallites with a typical size of 5.0 nm. Samples were patterned into Hall bridges using conventional UV lithography and plasma etching.

Measurements. The STM Pt/Ir tip was aligned above one of the free $500 \times 500\,\mu\mathrm{m}^2$ contact pads of the Hall bridge. In order to probe the local DOS, the differential conductance of the tunnel junction, $G(V) = dI/dV$, was measured by a lock-in amplifier technique with an alternative voltage of $10\,\mu$V added to the ramped bias voltage. The tunneling current was $0.5-1.0$ nA for milliVolts bias voltage yielding a tunneling resistance of about $1-2\,\mathrm{M}\Omega$, much higher than the sheet resistance of our samples. Hence, no voltage drop across the resistive film in series with the STM junction occurs during spectroscopy. Four probes measurements of the film resistance were carried out by acquiring both voltage and current with a low frequency lock-in amplifier technique in a four terminal configuration. Transport measurements and tunneling spectroscopy were systematically carried out during the same run in a home-built STM cooled down to 50 mK in a dilution refrigerator. Temperature of the sample holder, which was weakly coupled to the dilution refrigerator (30 nW of cooling power at $T = 100$ mK), was accurately controlled by a RuO_2 thermometer and a resistive heater. It is worth noticing that no measurable thermal drift of the tip position occurs in our STM between the base temperature of 50 mK and the highest measured temperature of about 6.3 K.

SUPPLEMENTARY INFORMATION

Thermal evolution of the density of states in bulk TiN

In moderately disordered bulk conventional superconductors, far from a disorder-tuned superconductor-insulator transition, the superconducting gap in the DOS vanishes right at the critical temperature T_c. In such superconductors the fluctuation regime is extremely small and no anomaly of the DOS is expected at the Fermi level above T_c. In figure 4, we present the thermal evolution of the tunneling conductance measured on a 100 nm thick TiN film. With a Drude resistance of $R_\square = 27\,\Omega$ and a superconducting critical temperature $T_c = 4.7$ K [5, 12], this sample can be considered as bulk TiN. As shown in figure 4, a flat metallic DOS is restored at low energy at T_c. This expected behaviour strongly contrasts with the pseudogaps observed in TiN1, TiN2 and TiN3.

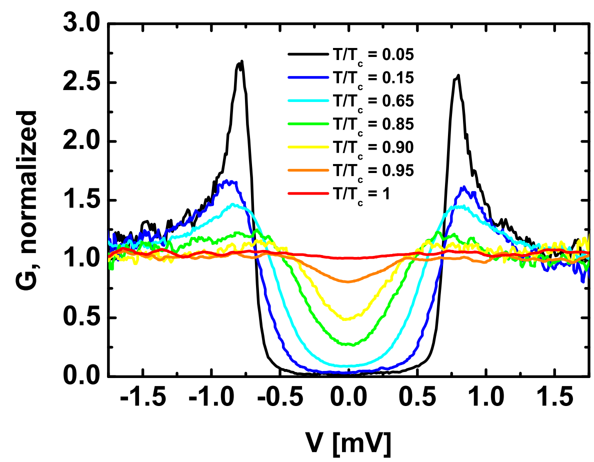

FIG. 4: Thermal evolution of the tunneling conductance measured on a thick TiN film with $T_c = 4.7$ K and $R_\square = 27\,\Omega$ (partly published in Ref. [12]).

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